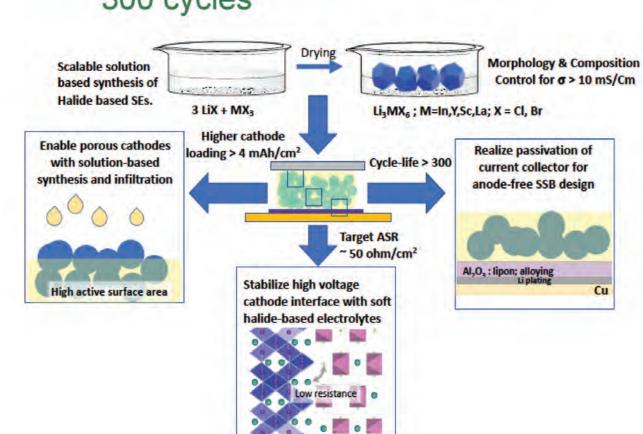
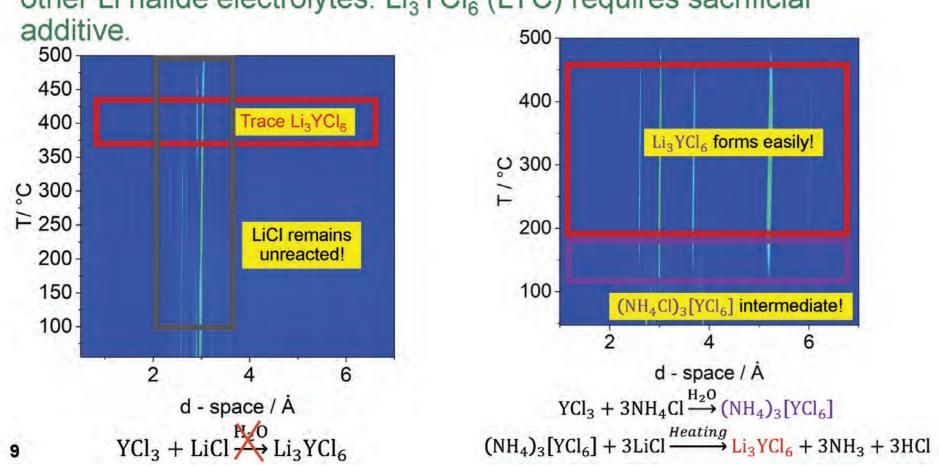


proach: The path towards sustainable 500 Wh/kg and 300 cycles

SSBs with Li metal anodes are key to enabling specific energies densities > 400 Wh/kg; however manufacturing and processing costs must be cost effective. This project focuses on synthesis of Li+ conducting halide-based solid electrolytes (SEs) and improving stability with high voltage cathodes.



TA: General solution based synthesis route does not work for other Li halide electrolytes. Li₃YCl₆ (LYC) requires sacrificial



Collaboration and Coordination with Other Institutions



Reviewer-Only Slides

Overview

<u>Timeline</u>

- Project start date: 10/1/2021

Project end date: 09/30/2026

• Percent complete: 25%

Budget

- FY22: \$250,000 • FY23: \$250,000

Barriers

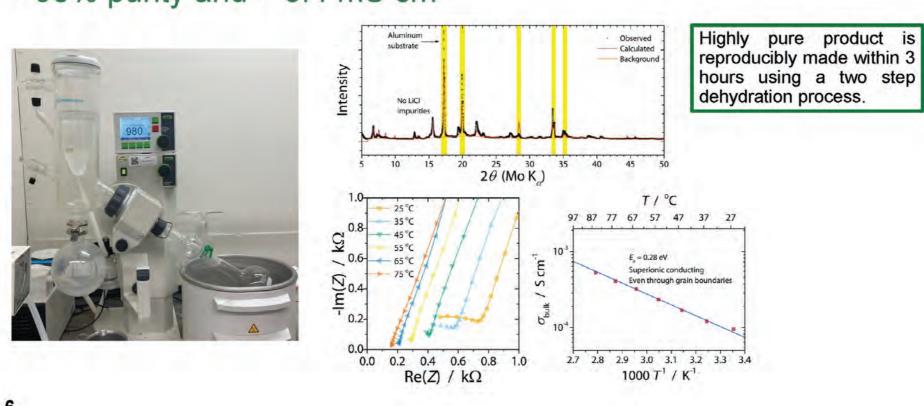
Performance: Demonstrating (i) SSBs with specific energy 500 Wh/kg over 1,000 cycles and (ii) solid electrolytes with ionic conductivity > 10⁻³ S/cm at room temperature Interfacial Stability: Developing low cost halide-based solid electrolytes that are stable against Li anodes and high voltage

Current Density: Achieving ≥2 mA/cm² at room temperature

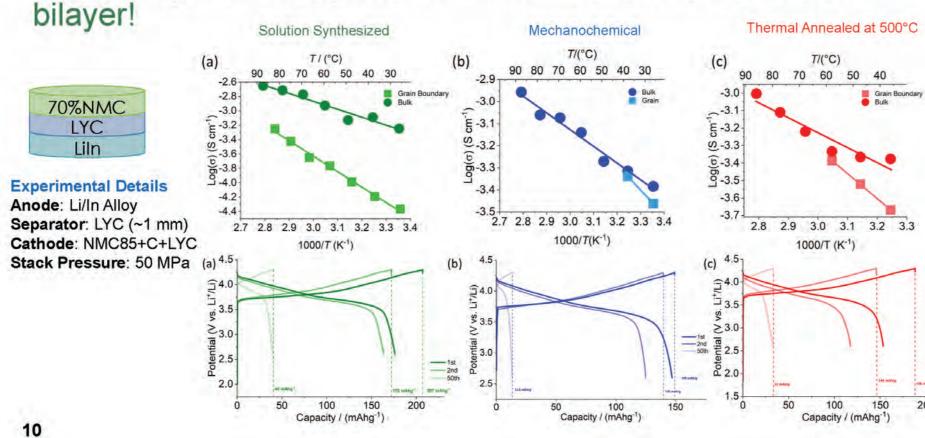
Partners/Collaborators

- University of Houston
- SLAC

FY22 Recap: Demonstrated the synthesis and scale up of Li₃InCl₆ (LIC) from alcohol and H2O solutions above 10 g with >95% purity and > 0.4 mS cm⁻¹



TA: Comparison of synthetic method for LYC shows that solution-synthesized performs better. None require LPSCI



Remaining Challenges and Barriers

- 1. Halide SE require high stack pressures to enable cycling at room temperature. Strategies (e.g., cathode adhesion) need to be developed to reduce stack pressure to <10 MPa for practical devices.
- 2. Developing mechanically robust, thin SE separators at scale is critical for high energy density. Binder and solvent selection are critical to maintain high ionic conductivity and good interfacial stability. Strategies are needed to synthesize and process thin SE in a roll-to-roll line is needed.
- 3. We need to utilize novel *operando* methods to studying buried interfaces in SSBs to gain insights into interphase evolution and mechanical strain.

Any proposed future work is subject to change based on funding levels

Publications & Presentations – FY 21/22

Conferences & Technical Meetings

- 1. "How Halide sub-lattice affects Li ion transport in antiperovskites and solution phase synthesis of Li Halide electrolytes" R. Sacci and J. Nanda 242nd ECS Meeting, Atlanta GA (Invited)
- 2. "Substituted Argyrodites and halide-based solid electrolytes for all solid-state batteries" R. Sacci and J. Nanda ACS Fall 2022, Chicago IL (Invited)

Peer-Reviewed Journal Publications

Relevance

<u>Impact</u>

 Solid electrolytes (SEs) with high Li⁺ conductivity and that are able to form robust interfaces with electrodes are critical to enable Li metal solid-state batteries (SSBs) for EV applications. Success is the development of a pathway for low-cost roll-to-roll based synthesis/processing by address technical barriers for robust SEcathode interfaces and improved rate capabilities.

Objectives

8 lighter color.

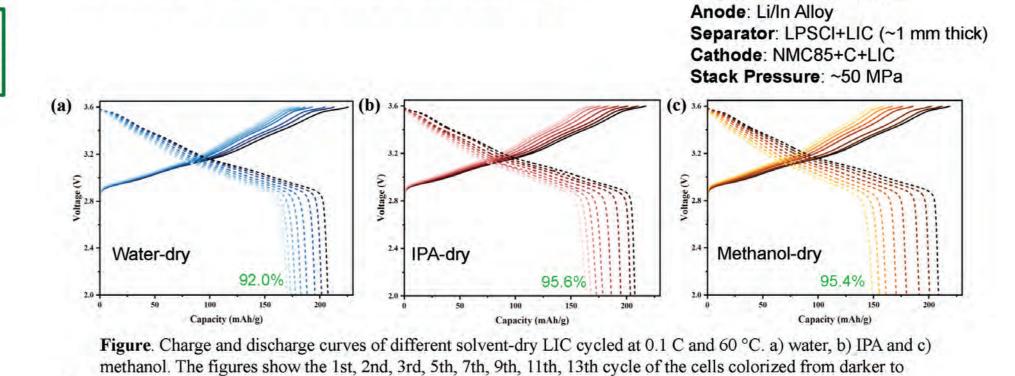
19

The goal is to develop inexpensive, solution-based methods that allow for growing halide-based solid electrolyte (SE) within the porous hi-voltage cathode matrix, leading to a drastic increase in the mechanical robustness and high-rate performance. A key objective is utilizing in situ electrochemical and scattering techniques to understand reaction pathways for optimizing ionic transport and interfacial adhesion.

Relevance to VTO Mission

R&D efforts on SEs and interfaces are critical to meet the VTO's long term goal of 500 Wh/kg and 1,000 cycles for EV applications.

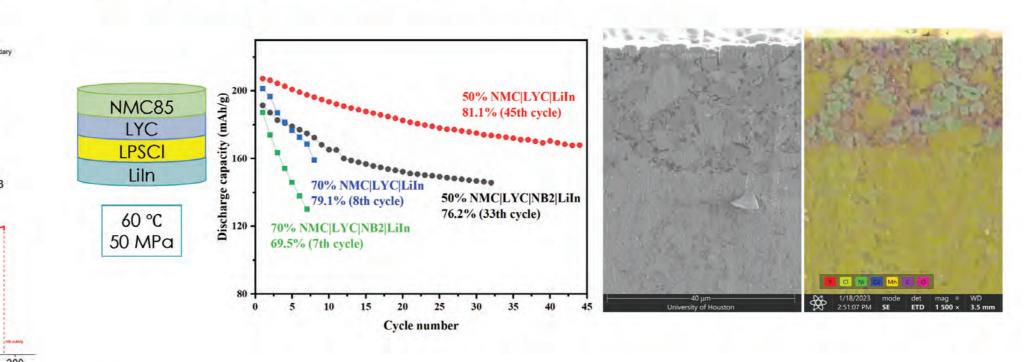
TA: Solution-based synthesis of Li3InCl6 can be expanded to alcohol to increase synthesis rate and decrease temperature required with little effect on cycling. **Experimental Details**



TA: LYC particles are larger than LIC, which means poorer

cathode loading. However, LYC does enable better cycling

performance without need of a buffer layer.



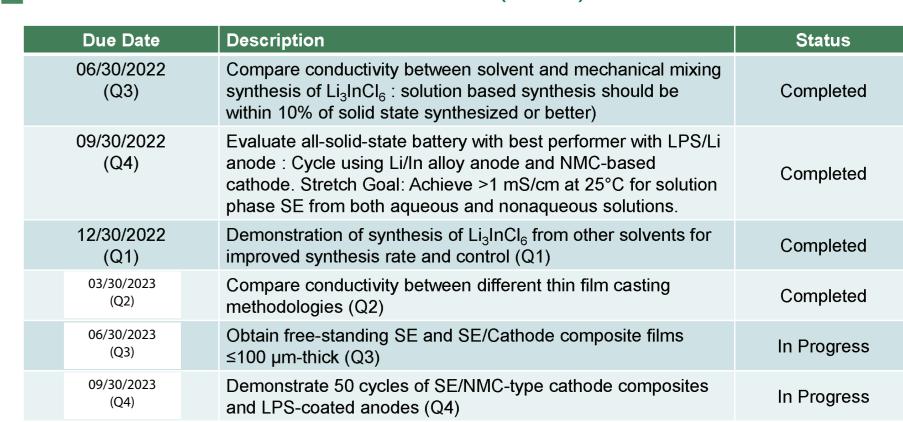
Proposed Future Research

- Improve chemical and redox stability of Li-halide SEs by partial substitution with halides and transition metal cations.
- Optimize composition and architecture of high voltage NMC cathodes that operate at voltages (>4 V vs. Li/Li⁺). Test other low-cobalt Li-ion cathodes such as disordered rocksalt (DRX) cathodes in solid-state batteries.
- Optimize slurry casting procedures to produce sulfide SE layers ≤ 50 µm thick. Thin separators are critical to attain high cell-level energy densities.
- 4. Demonstrate > 2 mA/cm² lithium plating and stripping by optimizing LI-halide SE-Li/In interphase and cell design
- Design < 1 µm thick protective interlayer to enable Li metal anodes.
- Any proposed future work is subject to change based on funding levels

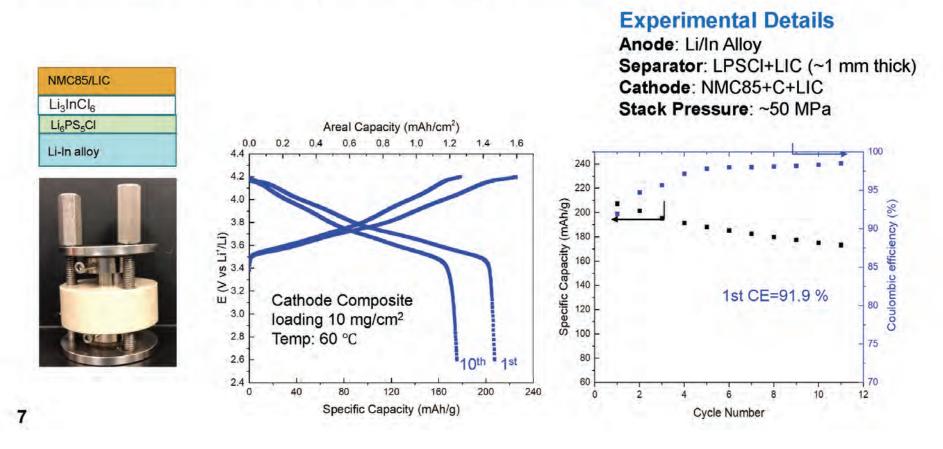
Critical Assumptions & Issues

- 1. Lithium Halide-based SEs have high Li⁺ conductivity and are readily synthesizable, but they have narrow electrochemical stability windows, especially on the anodic side. Passive does not occur naturally at the anode/electrolyte interfaces. Strategies to stabilize the electrode/electrolyte interfaces include: (i) adding buffer layers to mitigate SE decomposition and (ii) developing bilayer SE separators which enable independent optimization of Li/SE and cathode/SE interfaces.
- 2. Thin SE layers (≤ 50 µm) are critical to achieve high cell-level energy density. The impact of SE thickness and Li excess on cell performance needs to be studied in more detail. Especially when synthesized particles are 10s of microns in size.
- 3. Electrification of vehicles require SSBs with areal capacities ~5 mAh/cm² that are able to operate at ~10 mA/cm² for 1.000 cycles. Most SEs do not vet meet these criteria.
- 4. Costs will be a major market driver. Robust, thin and in expensive solid electrolytes are needed as well as rapid methods for joining the various electrodes together.

Milestones: FY-22 (Q3-4) and FY-23



Technical Accomplishments: Bilayer halide/argyrodite electrolyte enables cycling of high voltage, low cobalt NMC85.



Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Summary

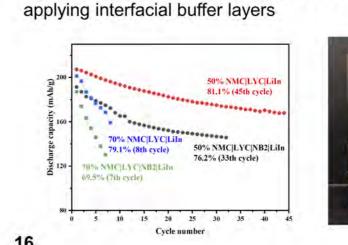
Technical Approach:

12

 Developed solution-based synthesis routes to produce superior Li-halide based solid electrolytes.

Accomplishments: Systematic investigation on synthesis of Li₃InCl₆ and its affects on full

- cell cycling performance. SSB performance is bottlenecked by cathode electrolyte interface and Li
- NMC|LYC|Li/In SSBs exhibit stable performance over 50 cycles without



· Optimize particle size and cathode distribution. Produce thin (<100 µm) halide SE separators

Frequency (Hz)

using tape-casting methods